Hylleraas and Kinoshita wave functions: Revision and correction

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As is the case of the Hylleraas six-term wave function, it is shown that several Hylleraas and Kinoshita wave functions for two-electron atoms given in the literature are not sufficiently accurate particularly in their exponents ζ. For example, Kinoshita reported that his 80-term helium wave function has the minimum energy of $-2.903\,723\,7$ a.u. for $\zeta = 1.855\,199$, while we obtain $-2.903\,724\,347$ a.u. for $\zeta = 2.245\,896$.

In a very recent paper,[1] it has been reported that the known parameter values[2–5] for the familiar Hylleraas six-term wave function[3–9] for the helium atom,

$$\Psi_6 = \exp(-\zeta s)(1 + c_1 u + c_2 t^2 + c_3 s + c_4 s^2 + c_5 u^2), \tag{1}$$

are not as accurate as previously believed, and accordingly the wave function (1) can have an energy lower than the value hitherto given in the literature[3–9] by about 0.0001. (Atomic units are used throughout.) Comparison of the new and literature parameters has shown[1] that the essential origin of the energy improvement lies in the value of the exponent ζ, and sufficient optimization of this nonlinear parameter has been suggested to be crucial for the accurate determination of the wave function and the associated energy.

Stimulated by the above result, we have considered it necessary to reconfirm other (more elaborate) Hylleraas wave functions reported in the literature,[10–12] since they are often used as parent functions to derive physical quantities of near exact accuracy (see, e.g., Refs. 13 and 14). Similar examination has also been carried out for the Kinoshita wave functions.[15,16] Unfortunately, we have to report in this article that the known parameters and associated energies are insufficiently accurate for both the Hylleraas and Kinoshita wave functions.

The Hylleraas and Kinoshita wave functions for ground state two-electron atoms are generally given by

$$\Psi_N = \exp(-\zeta s) \sum_{i=1}^{N} c_i s^{l_i} t^{2m_i} u^{n_i}, \tag{2a}$$

$$\Psi_N = \exp(-\zeta s) \sum_{i=1}^{N} c_i s^{l_i} (u/s)^{m_i} (t/u)^{2n_i}, \tag{2b}$$

respectively, where $s = r_1 + r_2$, $t = r_1 - r_2$, and $u = r_{12}$ are Hylleraas coordinates, $\{l_i, m_i, n_i\}$ are non-negative integers, and ζ and $\{c_i\}$ are variational parameters.

The two-electron atomic Hamiltonian in the Hylleraas coordinates is given elsewhere.[2,6,7,17] For the trial functions (2a) and (2b), we can express all the Hamiltonian H_{ij} and overlap S_{ij} matrix elements in terms of a basic integral (cf. Ref. 11),

$$\int_0^\infty ds \int_0^s dt \int_t^s du \exp(-2\zeta s) s^I t^J u^K = (I+J+K+2)!/[(2\zeta)^{I+J+K+3} \times (J+1)(J+K+2)]. \tag{3}$$

The variation of the energy expression $E = \mathbb{C}^+\mathbb{H}\mathbb{C}/\mathbb{C}^+\mathbb{S}\mathbb{C}$ with respect to the linear parameters $\{c_i\}$ results in an eigenvalue equation $\mathbb{H}\mathbb{C} = \mathbb{S}\mathbb{C}E$. Then using an appropriate routine program of the generalized eigenvalue equation solver,[18] we can accurately determine the energy E and the expansion coefficients $\{c_i\}$ for a given value of ζ. For the determination of the nonlinear parameter ζ, we have employed two different methods in order to check its optimality and accuracy. One method finds the optimum ζ by the minimization of E

TABLE I. Energy E and exponent ζ of several Hylleraas wave functions of the helium atom.

	Literature			Present	
N	E	ζ	Ref.	E	ζ
6	$-2.903\,24$	1.82	2	$-2.903\,329\,354$[a]	1.755 656[a]
10	$-2.903\,602\,7$	1.755 013	10	$-2.903\,602\,729$	1.757 763
14	$-2.903\,701$	1.90	11	$-2.903\,701\,491$	1.897 917
18	$-2.903\,71$[b]	1.925	11	$-2.903\,716\,636$	1.938 541
	$-2.903\,715\,0$	1.944 606	15		
20	$-2.903\,717\,9$	1.935	12	$-2.903\,717\,754$	1.932 909
	($-2.903\,717\,733$[c])				

[a] Reference 1.
[b] In Ref. 11, the energy $-2.903\,716$ is also given for the 18-term function. However, it is not included in this table since no corresponding wave function is reported.
[c] Recalculated based on the parameters given in Ref. 12.

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TABLE II. The Hyllerass 20-term energy for the helium atom as a function of the exponent ζ around its optimum value. The linear parameters $\{c_i\}$ are optimized for each ζ value.

ζ	E	$-V/T$
1.925	−2.903 717 736	2.000 003 108
1.926	−2.903 717 740	2.000 002 729
1.927	−2.903 717 744	2.000 002 346
1.928	−2.903 717 747	2.000 001 959
1.929	−2.903 717 750	2.000 001 568
1.930	−2.903 717 752	2.000 001 173
1.931	−2.903 717 753	2.000 000 774
1.932	−2.903 717 754	2.000 000 370
1.933[a]	−2.903 717 754	1.999 999 963
1.934	−2.903 717 754	1.999 999 551
1.935[b]	−2.903 717 753	1.999 999 135
1.936	−2.903 717 751	1.999 998 714
1.937	−2.903 717 749	1.999 998 290
1.938	−2.903 717 746	1.999 997 861
1.939	−2.903 717 743	1.999 997 427
1.940	−2.903 717 739	1.999 996 990

[a] This ζ is closest to the present optimum value in this table.
[b] The ζ value of Hart and Herzberg (Ref. 12).

based on the Powell method of conjugate directions.[19] The other method determines the parameter ζ iteratively so that the virial theorem[20] is satisfied, i.e., $V=-2T$ or $E=-V^2/4T$ holds, where T and V are the kinetic and potential energy components. (Note that in the above procedures of ζ optimization, all the $\{c_i\}$ are variationally determined for each value of ζ.)

Table I compares the present results for the Hylleraas 10-, 14-, 18-, and 20-term wave functions with those reported by Herzberg and co-workers.[10–12] (The $\{c_i\}$ are omitted there, but they are available upon request.) The energies for $N=10$ and 14 in the literature agree with the present values within the given decimal places. A non-negligible improvement is found for the energy of $N=18$. In the case of $N=20$, however, the literature energy value[12] is lower than that we obtained. We were not able to reproduce the literature value even when we input the corresponding parameters reported in Ref. 12: It is suggested that the energy interpolation used in the literature is not sufficiently accurate. In Table II, we have explicitly given the minimum energy as a function of the exponent ζ around its optimun value. The very weak dependence of the energy upon this parameter is observed.

TABLE III. Energy E and exponent ζ of several Kinoshita wave functions for the helium atom.

	Literature			Present	
N	E	ζ	Ref.	E	ζ
10	−2.903 626 1	1.729 575	15	−2.903 627 336	1.745 726
22	−2.903 714 2	1.853 910	15	−2.903 718 784	1.812 833
34	−2.903 722 3	1.856 694	15	−2.903 722 780	2.021 305
38	−2.903 722 5	1.860 237	15	−2.903 722 839	2.028 535
39	−2.903 722 5	1.860 556	15	−2.903 722 910	1.996 338
80	−2.903 723 7	1.855 199	16	−2.903 724 347	2.245 896

TABLE IV. The Kinoshita 80-term energy for the helium atom as a function of the exponent ζ around its optimum value. The linear parameters $\{c_i\}$ are optimized for each ζ value.

ζ	E	$-V/T$
1.80	−2.903 724 265	2.000 000 263
1.82	−2.903 724 273	2.000 000 244
1.84	−2.903 724 280	2.000 000 226
1.86[a]	−2.903 724 287	2.000 000 210
1.88	−2.903 724 293	2.000 000 195
1.90	−2.903 724 299	2.000 000 182
1.92	−2.903 724 305	2.000 000 169
1.94	−2.903 724 309	2.000 000 157
1.96	−2.903 724 314	2.000 000 146
1.98	−2.903 724 318	2.000 000 136
2.00	−2.903 724 322	2.000 000 127
2.02	−2.903 724 325	2.000 000 118
2.04	−2.903 724 329	2.000 000 109
2.06	−2.903 724 332	2.000 000 101
2.08	−2.903 724 334	2.000 000 094
2.10	−2.903 724 337	2.000 000 086
2.12	−2.903 724 339	2.000 000 079
2.14	−2.903 724 341	2.000 000 070
2.16	−2.903 724 343	2.000 000 062
2.18	−2.903 724 345	2.000 000 051
2.20	−2.903 724 346	2.000 000 039
2.22	−2.903 724 347	2.000 000 025
2.24[b]	−2.903 724 347	2.000 000 006
2.26	−2.903 724 347	1.999 999 983
2.28	−2.903 724 346	1.999 999 954
2.30	−2.903 724 344	1.999 999 916

[a] This ζ value is closest to the Kinoshita value (Ref. 16) in this table.
[b] This ζ value is closest to the present optimum value in this table.

Though the change in the energy value is relatively small, the optimum values for the nonlinear parameter ζ are found to be considerably different except for the 14-term function. The difference in the exponent ζ implies the difference in the coefficients $\{c_i\}$, and hence a nontrivial change in the wave function Ψ_N. Since the change in the wave function linearly affects the resultant physical properties other than the total energy E, we expect a significant change in the calculated properties. For example, Benesch[14] constructed the radial electron density $D(r)$ based on the 20-term function reported by Hart and Herzberg[12] in the form of

$$D(r)=\exp(-2\zeta r)\sum_i a_i r^i+\exp(-4\zeta r)\sum_i b_i r^i. \qquad (4)$$

For the He atom, his first three a_i's are[14] 3.316 169, 40.657 413, and −8.027 578, but the present wave function gives 3.304 513, 40.668 878, and −8.196 001. He also reported[14] the electron–nuclear cusp constant $C_{EN}=2.002\,967$ and the virial ratio[21] $-V/T=1.999\,998\,869$, but we have $C_{EN}=2.002\,765$ and $-V/T=2.000\,000\,000$ from the present 20-term wave function. (The exact values are $C_{EN}=-V/T=2$ for the He atom.)

Our results for the several Kinoshita wave functions are summarized in Table III in comparison with the literature values.[15,16] The energies are seen to be improved for all cases, particularly for the 10- and 22-term wave functions. We also find that the Kinoshita 80-term function has an energy much closer to the "exact" value[22,23] −2.903 724 377 than hitherto believed. In contrast to the rather small change in the energy, the difference in the optimum exponent ζ is quite

remarkable. Table IV shows the explicit dependence of the energy upon the exponent ζ for the Kinoshita 80-term wave function. As has been exemplified for the Hylleraas 20-term wave function, we anticipate that the change in the wave function will give a nontrivial influence to the calculated physical properties.

We hope that the present report will be of some help to the future studies on two-electron atoms based on the Hylleraas- and Kinoshita-type wave functions.

Note added in proof. After this paper was accepted for publication, Professor A. J. Thakkar kindly informed me that P. Jolly [Int. J. Quantum Chem. **16**, 1149 (1979)] had reported a similar improvement of the Hylleraas wave function for the helium six-term case.

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